

## PCT REQUEST

PPC10801/UH

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0	For receiving Office use only	
0-1	International Application No.	PCT/FI 99 / 0 0 8 1 8
0-2	International Filing Date	0 5 OCT 1999 ( 0 5. 10. 99 )
0-3	Name of receiving Office and "PCT International Application"	The Finnish Patent Office PCT International Application
0-4	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.84 (updated 01.07.1999)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	National Board of Patents and Registration (Finland) (RO/FI)
0-7	Applicant's or agent's file reference	PPC10801/UH
I	Title of invention	METHOD AND DEVICE FOR SPRAYING OF A MATERIAL
II	Applicant	
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## PCT REQUEST

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<b>V</b>	<b>Designation of States</b>	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW SD SL SZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT  EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT  EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT  OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT

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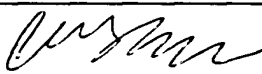
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<b>V-2</b>	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<b>AE AL AM AT (patent and utility model)</b> <b>AU AZ BA BB BG BR BY CA CH&amp;LI CN CR CU</b> <b>CZ (patent and utility model) DE (patent and utility model) DK (patent and utility model) DM EE (patent and utility model) ES FI (patent and utility model)</b> <b>GB GD GE GH GM HR HU ID IL IN IS JP KE</b> <b>KG KP KR KZ LC LK LR LS LT LU LV MD MG</b> <b>MK MN MW MX NO NZ PL PT RO RU SD SE SG</b> <b>SI SK (patent and utility model) SL TJ</b> <b>TM TR TT TZ UA UG US UZ VN YU ZA ZW</b>	
<b>V-5</b>	<b>Precautionary Designation Statement</b> In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
<b>V-6</b>	<b>Exclusion(s) from precautionary designations</b>	<b>NONE</b>	
<b>VI-1</b>	<b>Priority claim of earlier national application</b>		
VI-1-1	Filing date	<b>05 October 1998 (05.10.1998)</b>	
VI-1-2	Number	<b>982154</b>	
VI-1-3	Country	<b>FI</b>	
<b>VI-2</b>	<b>Priority document request</b> The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	<b>VI-1</b>	
<b>VII-1</b>	<b>International Searching Authority Chosen</b>	<b>Swedish Patent Office (ISA/SE)</b>	
<b>VIII</b>	<b>Check list</b>	number of sheets	electronic file(s) attached
VIII-1	Request	<b>4</b>	-
VIII-2	Description	<b>6</b>	-
VIII-3	Claims	<b>2</b>	-
VIII-4	Abstract	<b>1</b>	<b>ppc10801.txt</b>
VIII-5	Drawings	<b>1</b>	-
VIII-7	<b>TOTAL</b>	<b>14</b>	

## PCT REQUEST

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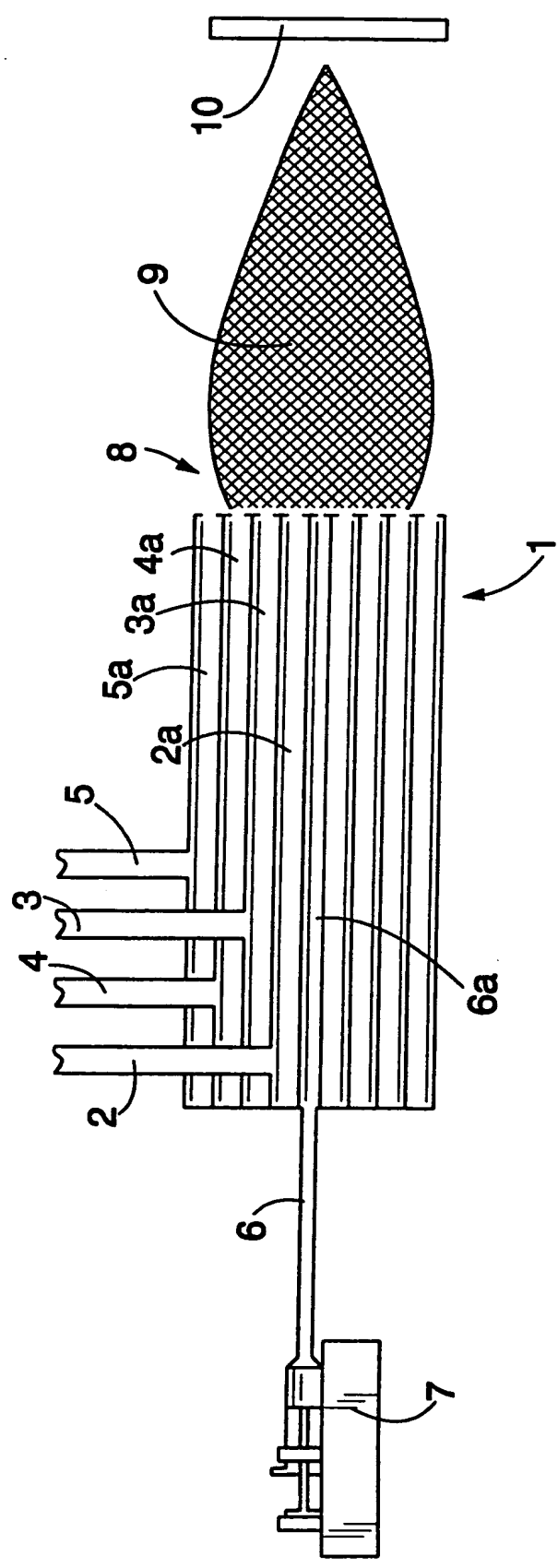
	Acc mpanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-17	Other (specified):	copy of Office Action	-
VIII-18	Figure of the drawings which should accompany the abstract	1	
VIII-19	Language of filing of the international application	Finnish	
IX-1	Signature of applicant or agent		
IX-1-1	Name	TAMPEREEN PATENTTITOIMISTO OY	
IX-1-2	Name of signatory	Unto Hakola	

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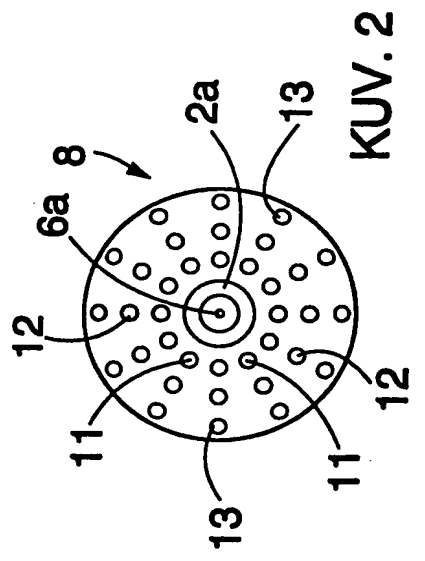
10-1	Date of actual receipt of the purported international application	0 5 OCT 1999 ( 0 5 -10- 1999 )
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/SE
10-6	Transmittal of search copy delayed until search fee is paid	X

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11-1	Date of receipt of the record copy by the International Bureau	2 7 OCTOBER 1999 ( 2 7. 10. 99 )
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KUV. 1



KUV. 2

## MENETELMÄ JA LAITE MATERIAALIN RUISKUTTAMISEKSI

Keksinnön kohteena on menetelmä materiaalin ruiskuttamiseksi, jossa menetelmässä muodostetaan liekki polttokaasun avulla, johdetaan liekkiin  
5 ainakin kahta erilaista komponenttia siten, että komponentit yhdistyvät keskenään ja muodostavat ainakin kahdesta komponentista koostuvaa materiaalia.

Edelleen keksinnön kohteena on laite materiaalin ruiskuttamiseksi, jossa laitteessa on välineet polttokaasun johtamiseksi siten, että polttokaasu muodostaa liekin ja välineet ainakin kahden erilaisen komponentin johtami-  
10 seksi liekkiin siten, että komponentit yhdistyvät keskenään ja muodostavat ainakin kahdesta komponentista koostuvaa materiaalia, jotka liekin avulla saadaan ruiskutettua haluttuun kohteeseen.

On tunnettua ruiskuttaa kiinteää ainetta liekkiruiskutuslaitteistolla. Kyseisessä menetelmässä ruiskutettava aine syötetään liekkiruiskuun kiinteinä  
15 hiukkasina, jotka liekkiruiskutuslaitteella ruiskutetaan haluttuun kohteeseen. Hiukkaskoon pienentyessä likaantuu ja tukkiintuu liekkiruiskutuslaitteisto kuitenkin helposti. Niinpä jo esimerkiksi alle 20 mikrometrin kokoisten hiukkasten ruiskuttaminen liekkiruiskutuslaitteistolla on hankalaa ja liekkiruiskutuslaitteisto tukkiintuu helposti ja on rakenteeltaan kallis. Edelleen ruiskutettava kiinteä on  
20 liekkiruiskutuksen aikana useassa eri faasissa ollen osaksi höyryä osaksi sulaa ainetta ja osittain sulanutta ainetta ja aineen jäähtyessä lopputulos on epätasainen.

US-patentissa 3 883 336 on esitetty laitteisto, jossa liekkiruiskuun tuodaan piitetrakloridia sumuna kantokaasuna toimivan hapen avulla. Edelleen  
25 kyseisessä julkaisussa on esitetty, että liekkiruiskun liekkiin suihkutetaan ulkopuolelta aerosolia lasin valmistamiseksi. Aerosolin tuottaminen vaatii kuitenkin monimutkaisen laitteiston ja edelleen aerosolin muodostaminen vaatii erityisesti nesteen viskositeetin olemista tietyissä rajoissa, mikä rajoittaa käytettäviä materiaaliyhdistelmiä. Edelleen menetelmällä tuotetut hiukkaset ovat varsin  
30 suurikokoisia eli noin mikrometrin suuruusluokkaa.

FI-patentissa 98832 on esitetty menetelmä ja laite materiaalin ruiskuttamiseksi, jossa menetelmässä ruiskutettava nestemäinen aine johdetaan polttokaasun avulla muodostettuun liekkiin ja pisaroitetaan kaasun avulla olennaisesti liekin läheisyydessä siten, että pisaroitus ja liekin muodostus ta-  
35 pahtuvat samassa laitteessa. Kyseisellä menetelmällä saadaan nanometrinen suuruus hiukkasla tuotettua yksinkertaisesti ja edullisesti. Ratkaisulla ei kui-

tenkaan pystytä tekemään useasta komponentista koostuvaa materiaalia, esimerkiksi monikomponenttilasia, jonka koostumus olisi hallittu.

Eräs sovellutus monikomponenttilasin tekemisestä on aktiivikuitujen tuotanto. Aktiivikuidun tuotannossa lasimateriaalia tulee seostaa harvinaisilla maametalleilla, esimerkiksi erbiümilla. Erbiümia ei ole saatavissa nesteinä, jonka höyrynpaine olisi riittävän alhainen siten, että aktiivikuituja voitaisiin tuottaa perinteisillä kuiduntuotantomenetelmillä ilman prosessin huomattavaa ja kallista modifiointia. Tämän vuoksi yleisesti käytetty menetelmä aktiivikuidun tuottamiseksi on valmistaa huokoinen, olennaisesti amorfisesta piidioksidista koostuva preformi, joka upotetaan erbiümia sisältävään nesteeseen. Usean tunnin imeytymisen jälkeen preformi kuivataan ja sintrataan, jolloin saadaan aikaan seostettu kuitupreformi. Menetelmän heikkoutena on aikaan saatavan seostusmäärän epämääräisyys ja aineen klusteroituminen, joka heikentää saatavan lopputuotteen ominaisuuksia. Edelleen aktiivikuitua voidaan valmistaa aerosoliprosessilla, missä erbiümpitoista aerosolia tuotetaan ultraäänimenetelmällä. Erikseen ultraäänimenetelmällä tuotetut aerosolit johdetaan termiseen reaktoriin, jossa ne reagoivat muodostaen monikomponenttilasia. Tämän menetelmän heikkoutena on sen monimutkaisuus, seostuksen hankaluus ja aikaansaatavien hiukkasten suuri koko, eli hiukkaset ovat noin mikrometrin suuruusluokkaa.

Tämän keksinnön tarkoituksena on saada aikaan menetelmä ja laitteisto, joissa edellä mainittuja epäkohtia pystytään välttämään.

Keksinnön mukaiselle menetelmälle on tunnusomaista se, että ensimmäinen komponentti johdetaan liekkiin kaasumaisessa tai höyrymäisessä muodossa ja toinen komponentti johdetaan liekkiin nestemäisessä muodossa ja pisaroitetaan jonkin kaasun avulla olennaisesti liekin läheisyydessä ja että sekä ensimmäinen komponentti että toinen komponentti syötetään liekkiin samalla laitteella polttokaasun kanssa.

Edelleen keksinnön mukaiselle laitteelle on tunnusomaista se, että laitteessa on kaasuputki ensimmäisen komponentin johtamiseksi liekkiin kaasumaisessa tai höyrymäisessä muodossa, nesteputki toisen komponentin johtamiseksi liekkiin nestemäisessä muodossa ja kaasuputki pirskotuskaasun johtamiseksi nesteputken läheisyyteen nestemäisen komponentin pisaroittamiseksi olennaisesti liekin läheisyydessä, jolloin sekä ensimmäinen komponentti että toinen komponentti on sovitettu syötettäväksi liekkiin samalla laitteella polttokaasun kanssa.

Keksinnön olennainen ajatus on, että liekkiin johdetaan ainakin kahta eri komponenttia ja että ensimmäinen komponentti johdetaan liekkiin kaasuna tai höyrynä ja toinen komponentti johdetaan liekkiin nestemäisessä muodossa ja pisaroitetaan kaasun avulla olennaisesti liekin läheisyydessä ja että ensimmäinen ja toinen komponentti syötetään liekkiin yhdessä polttokaasun kanssa samalla laitteella. Tällöin nestemäisestä komponentista ja kaasumaisesta komponentista muodostetaan suuruusluokaltaan nanometrin suuruisia hiukkasia ja saadaan aikaan näiden keskinäinen reaktio siten, että muodostuu esimerkiksi homogeenisia monikomponenttilasihiukkasia. Aikaansaadut hiukkaset voidaan edelleen ohjata liekin avulla eri materiaalien pinnalle tai kerätä erillisinä hiukkasina sopivalla laitteistolla esimerkiksi aktiivikuidun valmistamiseksi.

Keksinnön etuna on, että pystytään erittäin yksinkertaisesti ja edullisesti tuottamaan erittäin pieniä ja homogeenisia ainakin kahdesta komponentista koostuvia hiukkasia, kuten monikomponenttilasihiukkasia.

Keksintöä selitetään tarkemmin oheisessa piirustuksessa, jossa kuvio 1 esittää kaavamaisesti keksinnön mukaista liekkiruiskutuslaitteiston kokonaisuutta sivustapäin katsottuna ja

kuvio 2 esittää kaavamaisesti kuvion 1 mukaisen laitteen suutinosaa edestäpäin katsottuna.

Kuviossa 1 on esitetty keksinnön mukainen liekkiruiskutuslaitteisto. Liekkiruiskulla 1 muodostetaan liekki 9 ruiskutettavan aineen ruiskuttamiseksi. Liekkiruiskuun 1 tuodaan tarvittavat kaasut kaasukanavia 2, 3, 4 ja 5 pitkin. Kaasukanavia 2 - 5 pitkin tuodaan liekin muodostavat polttokaasut, ruiskutettavan nesteen pirskotuskaasu, muodostettavan, ainakin kahdesta komponentista koostuvan materiaalin, kuten monikomponenttilasin, eräs komponentti kaasu- tai höyrymuodossa ja mahdollinen reaktion hallintaa varten tuotettava kaasu. Kaasukanavia 2 - 5 on luonnollisesti tarpeellinen määrä sen mukaan kuinka monta kaasua liekkiruiskuun 1 on tarpeen syöttää. Muodostettavan monikomponenttilasin toinen komponentti syötetään nestemäisessä muodossa liekkiruiskuun 1 nestekanavaa 6 pitkin. Neste siirretään nestekanavaa 6 pitkin pumppaamalla sitä esimerkiksi ruiskupumpulla 7. Nesteen siirtyminen nestekanavaa 6 pitkin voidaan toteuttaa myös esimerkiksi syöttämällä neste painesäiliöstä tai jollain muulla sinänsä tunnetulla tavalla.

Liekkiruiskun 1 kuviossa 1 katsottuna oikeassa päädyssä on suutin 8, jossa polttokaasut sytytetään liekin aikaansaamiseksi ja jossa neste pisaroitetaan pirskotuskaasun avulla, jolloin pirskotus tapahtuu olennaisesti liekin 9



läheisyydessä. Tällöin nestemäinen komponentti saadaan pisaroitettua erittäin pi niksi suuruusluokaltaan noin nanometrin suuruiseksi hiukkasiksi. Samoin kaasumaisesta tai höyrymäisestä komponentista saadaan muodostettua yhtä pieniä hiukkasia. Kummatkin komponentit syötetään liekkiin yhdessä poltto-  
5 kaasun kanssa samalla laitteella. Edullisimmin polttokaasun syöttö, ensimmäisen komponentin syöttö ja toisen komponentin syöttö liekkiin toteutetaan yhdellä ja samalla laitteella eli yhteisen suuttimen 8 kautta, kuten kuviossa 1 on esitetty. Tällöin ruiskutettavien monikomponenttilasihiukkasten kohdistaminen kohteeseen 10 on erittäin helppoa. Ensimmäisen ja toisen komponentin hiuk-  
10 kaset reagoivat keskenään muodostaen homogeenisia monikomponenttilasihiukkasia. Monikomponenttilasihiukkaset voidaan edelleen ohjata liekin 9 avulla eri materiaalien pinnalle tai kerätä erillisinä hiukkasina sopivalla laitteistolla.

Monikomponenttilasin nestemäinen komponentti tuodaan liekkiruiskun 15 kuun 1 nestekanavaa 6 pitkin. Nestekanavasta 6 neste siirtyy liekkiruiskun 1 keskellä olevaan nesteputkeen 6a. Ensimmäistä kaasukanavaa 2 pitkin johdetaan nesteen pirs-kottava kaasu nesteputken ympärillä olevaan ensimmäiseen kaasuputkeen 2a. Toista kaasukanavaa 3 pitkin johdetaan toinen kaasu ensimmäisen kaasuputken 2a ympärillä olevaan toiseen kaasuputkeen 3a.  
20 Edelleen kolmatta kaasukanavaa 4 pitkin johdetaan kolmas kaasu toisen kaasuputken 3a ympärillä olevaan kolmanteen kaasuputkeen 4a ja neljättä kaasukanavaa 5 pitkin johdetaan neljäs kaasu kolmannen kaasuputken 4a ympärillä olevaan neljänteen kaasuputkeen 5a. Nesteputki 6a ja ensimmäinen, toinen, kolmas ja neljäs kaasuputki 2a, 3a, 4a, ja 5a ovat siis koaksiaalisia sisä-  
25 käisiä putkia. Suuttimessa 8 ensimmäisestä kaasuputkesta 2a tuleva kaasu pisaroittaa nesteputkea 6a pitkin tulevan nesteen pisaroiksi.

Muodostettavan monikomponenttilasin nestemäinen komponentti voi olla sopiva halutun ionin vesi- tai alkoholiliuos. Esimerkiksi aktiivikuitua eli valoa vahvistavaa kuitua tuotettaessa voidaan käyttää liuosta, jossa on erbiu-  
30 nitraattia, vettä tai alkoholia ja jotain alumiinin muotoa, joka liukenee veteen tai alkoholiin. Toista kaasukanavaa 2 pitkin voidaan syöttää esimerkiksi vetyä, joka pisaroittaa nesteen suuttimessa 8. Toista kaasukanavaa 3 pitkin voidaan syöttää pii- tai germaniumtetrakloridia kaasumaisessa tai höyrymäisessä muodossa ja kolmatta kaasukanavaa 4 pitkin happea. Suuttimen 8 jälkeen vety ja  
35 happi reagoivat muodostaen liekin 9. Liekin reaktiomuodostuksen tarkka prosessi on epäselvä, mutta käytännössä voidaan olettaa, että pii- tai germa-

niumtetrakloridi reagoi muodostaen erittäin pieniä piidioksidi- tai germaniumdioksidahiukkasia ja nestemäiset hiukkaset reagoivat muodostaen erbi- ja alumiinioksidia. Muodostuneet hiukkaset reagoivat joko samanaikaisesti tai erillisesti edellä mainittujen reaktioiden kanssa ja yhtyvät keskenään muodostaen homogeenista monikomponenttilasia. Syntyneet monikomponenttilasihiukkaset ohjataan liekin 9 avulla kohteen 10 pinnalle, joka aktiivikuitua valmistettaessa on tuurna, jolloin monikomponenttilasihiukkaset muodostavat tuurnan pinnalle huokoisen lasipinnan. Tuurnan pinnalle voidaan kasvattaa useita eri lasikerroksia, joiden materiaali koostumusta voidaan haluttaessa yksinkertaisesti muuttaa. Kasvatuksen jälkeen tuurna voidaan poistaa ja muodostunut preformi sintrataan normaalista optisen kuidun valmistusprosessista sinänsä tunnetulla tavalla.

Neljäs kaasukanava 5 ja vastaavasti neljäs kaasuputki 5a eivät ole välttämättömiä. Niitä voidaan kuitenkin haluttaessa käyttää reaktion hallinnan parantamiseksi esimerkiksi syöttämällä neljättä kaasukanavaa 5 ja edelleen neljättä kaasuputkea 5a pitkin esimerkiksi argonia tai jotain muuta sopivaa suojakaasua, jolloin suojakaasu estää ulkopuolisen hapen vaikutuksen reaktioon.

On huomattavaa, että kuviossa 1 on liekkiruiskun 1 rakenne esitetty selvytyden vuoksi todellista tilannetta suuremmassa mittakaavassa. Tehokkaan pisaroitumisen aikaansaamiseksi kannattaa esimerkiksi pirskotuskaasun nopeus saada mahdollisimman suureksi. Näin ollen suuttimen 8 reiät kannattaa tehdä riittävän pieniksi. Edelleen nesteputken 6a ja ensimmäisen kaasuputken 2a rakennetta voidaan kuvata siten, että kyseiset putket ovat rakenteeltaan kaksi onttoa sisäkkäin asetettua neulaa.

Kuviossa 2 on esitetty suutin 8 edestäpäin katsottuna. Kuviossa 2 näkyy suuttimen 8 keskeltä tulevan nesteputken 6a päädyssä oleva reikä. Sen ympärillä näkyy ensimmäisen kaasuputken 2a reikä. Toista kaasuputkea 3a pitkin tuleva kaasua on esitetty johdettavaksi suuttimen 8 läpi aukkojen 11 kautta. Vastaavasti kolmatta kaasuputkea 4a pitkin tuleva kaasua johdetaan suuttimen 8 läpi aukkojen 12 kautta ja neljättä kaasuputkea 5a pitkin tuleva kaasua johdetaan suuttimen 8 läpi aukkojen 13 kautta. Suuttimen 8 reikien ja aukkojen koko ja geometria voi vaihdella halutulla tavalla, mutta olennaista on, että suuttimessa 8 nesteen ja pirskotuskaasun nopeus saadaan halutunlaiseksi siten, että neste saadaan pisaroitettua riittävän pieneksi, jolloin saadaan aikaan riittävän pieniä hiukkasia ja että toisaalta liekin 9 muodostavien kaasujen

nopeus on riittävä.

Piirustus ja siihen liittyvä selitys on tarkoitettu vain havainnollistamaan keksinnön ajatusta. Yksityiskohdiltaan keksintö voi vaihdella patentti-  
vaatimusten puitteissa. Niinpä nesteputken ja kaasuputkien sijainti ja järjestys  
5 voi vaihdella halutulla tavalla. Edelleen polttokaasu voi muodostua edellä esi-  
tetyllä tavalla kahdesta tai useammasta, erillistä kaasuputkea pitkin suuttimelle  
8 syötettävästä, kaasusta tai sitten polttokaasuna voidaan käyttää suuttimelle  
8 yhtä kaasuputkea pitkin syötettävää kaasua tai kaasuseosta, kuten hapen ja  
asetyleenin seosta.

## PATENTTIVAATIMUKSET

1. Menetelmä materiaalin ruiskuttamiseksi, jossa menetelmässä muodostetaan liekki (9) polttokaasun avulla, johdetaan liekkiin (9) ainakin  
5 kahta erilaista komponenttia siten, että komponentit yhdistyvät keskenään ja muodostavat ainakin kahdesta komponentista koostuvaa materiaalia, t u n n e t t u siitä, että ensimmäinen komponentti johdetaan liekkiin (9) kaasumaisessa tai höyrymäisessä muodossa ja toinen komponentti johdetaan liekkiin (9) nestemäisessä muodossa ja pisaroitetaan jonkin kaasun avulla olennaisesti liekin (9) läheisyydessä ja että sekä ensimmäinen komponentti että toinen komponentti syötetään liekkiin (9) samalla laitteella polttokaasun kanssa.

2. Patenttivaatimuksen 1 mukainen menetelmä, t u n n e t t u siitä, että ensimmäinen komponentti, toinen komponentti ja polttokaasu syötetään liekkiin (9) samalla laitteella.

15 3. Patenttivaatimuksen 2 mukainen menetelmä, t u n n e t t u siitä, että ensimmäinen komponentti, toinen komponentti ja polttokaasu syötetään liekkiin (9) koaksiaalisesti.

4. Jonkin edellisen patenttivaatimuksen mukainen menetelmä, t u n n e t t u siitä, että ensimmäinen komponentti on pii- tai germaniumtetrakloridia  
20 ja toinen komponentti on liuosta, joka sisältää erbiumnitraattia, vettä tai alkoholia ja veteen tai alkoholiin liukenevaa alumiinin muotoa siten, että saadaan muodostettua monikomponenttilasihiukkasia aktiivikuidun valmistamiseksi.

5. Laite materiaalin ruiskuttamiseksi, jossa laitteessa on välineet polttokaasun johtamiseksi siten, että polttokaasu muodostaa liekin (9) ja välineet ainakin kahden erilaisen komponentin johtamiseksi liekkiin (9) siten, että komponentit yhdistyvät keskenään ja muodostavat ainakin kahdesta komponentista koostuvaa materiaalia, jotka liekin (9) avulla saadaan ruiskutettua haluttuun kohteeseen, t u n n e t t u siitä, että laitteessa on kaasuputki (3a) ensimmäisen komponentin johtamiseksi liekkiin (9) kaasumaisessa tai höyrymäisessä muodossa, nesteputki (6a) toisen komponentin johtamiseksi liekkiin (9) nestemäisessä muodossa ja kaasuputki (2a) pirstotuskaasun johtamiseksi nesteputken läheisyyteen nestemäisen komponentin pisaroittamiseksi olennaisesti liekin (9) läheisyydessä, jolloin sekä ensimmäinen komponentti että toinen komponentti on sovitettu syötettäväksi liekkiin (9) samalla laitteella  
35 polttokaasun kanssa.

6. Patenttivaatimuksen 5 mukainen laite, t u n n e t t u siitä, että

laitteessa on suutin (8) ja että laitteessa on välineet ensimmäisen komponentin, toisen komponentin ja polttokaasun syöttämiseksi liekkiin (9) yhteisen suuttimen (8) kautta.

- 5 7. Patenttivaatimuksen 6 mukainen laite, t u n n e t t u siitä, että välineet ensimmäisen komponentin, toisen komponentin ja polttokaasun syöttämiseksi liekkiin (9) on sovitettu koaksiaalisesti.

**(57) Tiivistelmä**

Keksinnön kohteena on menetelmä ja laite materiaalin ruiskuttamiseksi, jolloin ainakin kahta erilaista komponenttia johdetaan polttokaasun avulla muodostettuun liekkiin (9) siten, että komponentit reagoivat keskenään muodostaen monikomponenttilasihiukkasia. Liekin (9) avulla monikomponenttilasihiukkaset ruiskutetaan haluttuun kohteeseen. Ensimmäinen komponentti johdetaan liekkiin kaasuna tai höyrynä ja toinen komponentti johdetaan liekkiin nestemäisessä muodossa ja pisaroitetaan kaasun avulla olennaisesti liekin läheisyydessä. Ensimmäinen ja toinen komponentti syötetään liekkiin (9) yhdessä polttokaasun kanssa samalla laitteella, jolloin nestemäisestä komponentista ja kaasumaisesta komponentista muodostetaan suuruusluokaltaan nanometrin suuruisia hiukkasia ja saadaan aikaan näiden keskinäinen reaktio siten, että muodostuu homogeenisia monikomponenttilasihiukkasia.

(kuvio

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE

(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

TAMPEREEN PATENTTITOIMISTO OY  
Hermiankatu 6  
FIN-33720 Tampere  
FINLANDE

Date of mailing (day/month/year) 26 January 2001 (26.01.01)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference PPC10801/UH	
International application No. PCT/FI99/00818	International filing date (day/month/year) 05 October 1999 (05.10.99)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input type="checkbox"/> the inventor	<input type="checkbox"/> the agent
<input type="checkbox"/> the common representative		
Name and Address	State of Nationality	State of Residence
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input checked="" type="checkbox"/> the person	<input checked="" type="checkbox"/> the name	<input checked="" type="checkbox"/> the address
<input checked="" type="checkbox"/> the nationality	<input checked="" type="checkbox"/> the residence	
Name and Address LIEKKI OY Kivikonlaita 5 FIN-00940 Helsinki Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
3. Further observations, if necessary: <b>Please note new applicant for all designated States except US. RAJALA, Markku, EEROLA, Markus, TIKKANEN, Juha and PITKANEN, Ville remain inventors and applicants for US only.</b>		
4. A copy of this notification has been sent to:		
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned	
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned	
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:	

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Céline Faust
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

## PATENT COOPERATION TREATY

0 2. 02. 2001

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

TAMPEREEN PATENTTITOIMISTO OY  
Hermiankatu 6  
FIN-33720 Tampere  
FINLANDE

Date of mailing (day/month/year) 26 January 2001 (26.01.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference PPC10801/UH	
International application No. PCT/FI99/00818	International filing date (day/month/year) 05 October 1999 (05.10.99)

## 1. The following indications appeared on record concerning:

☒ the applicant      ☐ the inventor      ☐ the agent      ☐ the common representative

Name and Address	State of Nationality	State of Residence
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person      ☒ the name      ☒ the address      ☒ the nationality      ☒ the residence


Name and Address LIEKKI OY Kivikonlaita 5 FIN-00940 Helsinki Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 3. Further observations, if necessary:

**Please note new applicant for all designated States except US. RAJALA, Markku, EEROLA, Markus, TIKKANEN, Juha and PITKANEN, Ville remain inventors and applicants for US only.**

## 4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colmbettes 1211 Geneva 20, Switzerland  Facsimile No.: (41-22) 740.14.35	Authorized officer  Céline Faust   Telephone No.: (41-22) 338.83.38
--	--



RECEIVED

## PATENT COOPERATION TREATY

14.06.2000


**TAMPEREEN  
PATENTTITOIMISTO**
**PCT****INFORMATION CONCERNING ELECTED  
OFFICES NOTIFIED OF THEIR ELECTION**

(PCT Rule 61.3)

From the INTERNATIONAL BUREAU

To:

TAMPEREEN PATENTTITOIMISTO OY  
Hermiankatu 6  
FIN-33720 Tampere  
FINLANDE

Date of mailing (day/month/year) 30 May 2000 (30.05.00)		
Applicant's or agent's file reference PPC10801/UH		<b>IMPORTANT INFORMATION</b>
International application No. PCT/FI99/00818	International filing date (day/month/year) 05 October 1999 (05.10.99)	
Priority date (day/month/year) 05 October 1998 (05.10.98)		
Applicant RAJALA, Markku et al		

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

AP : GH,GM,KE,LS,MW,SD,SL,SZ,TZ,UG,ZW

EP : AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE

National : AU,BG,BR,CA,CN,CZ,DE,IL,JP,KP,KR,MN,NO,NZ,PL,RO,RU,SE,SK,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

EA : AM,AZ,BY,KG,KZ,MD,RU,TJ,TM

OA : BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG

National : AE,AL,AM,AT,AZ,BA,BB,BY,CH,CR,CU,DK,DM,EE,ES,FI,GB,GD,GE,GH,GM,  
HR,HU,ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MW,MX,PT,SD,SG,SI,  
SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No. (41-22) 740.14.35</p>	<p>Authorized officer: F. Baechler</p> <p>Telephone No. (41-22) 338.83.38</p>
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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PPC10801/UH	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/FI99/00818	International filing date (day/month/year) 05.10.1999	Priority date (day/month/year) 05.10.1998
International Patent Classification (IPC) or national classification and IPC <sub>7</sub> C03B 37/018		
Applicant (RAJALA, Markku et al) LIEKKI OY		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of <u>4</u> sheets, including this cover sheet.  <input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  These annexes consist of a total of _____ sheets.
3. This report contains indications relating to the following items:  I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application

Date of submission of the demand  02.05.2000	Date of completion of this report  19.12.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer  Mattias Arvidsson/MP Telephone No. 08-782 25 00

**I. Basis of the report****1. With regard to the elements of the international application:\***

- ☒ the international application as originally filed
- ☐ the description:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the claims:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, as amended (together with any statement) under article 19  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the drawings:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the sequence listing part of the description:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

**2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.**

These elements were available or furnished to this Authority in the following language English which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☒ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

**3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:**

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

**4. ☐ The amendments have resulted in the cancellation of:**

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims. Nos. \_\_\_\_\_
- ☐ the drawings, sheet/fig \_\_\_\_\_

**5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2 (c)).\*\***

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims	<u>1-7</u>	YES
	Claims		NO
Inventive step (IS)	Claims		YES
	Claims	<u>1-7</u>	NO
Industrial applicability (IA)	Claims	<u>1-7</u>	YES
	Claims		NO

**2. Citations and explanations (Rule 70.7)**

The claimed invention relates to a method and device for spraying of a material in which a flame is produced by means of a fuel gas, and at least two different components are introduced to the flame in such a way that the components combine with each other, and form a material consisting of at least two components.

The following documents cited in the international search report, are documents of particular relevance:

D1: JP 4021536 WPI Derwent Abstract  
D2: US 5246475

Document D1 relates to a method for producing glass doped with rare earth element by feeding raw material glass and rare earth chloride vapour into flame and spraying on to a rotating silica target rod.

Document D2 relates to Method for preparing a fused silica glass body co-doped with a rare earth element and aluminium

Claims 1-3 and 5-7

Document D1 discloses feeding a glass starting material and atomised rare earth chloride hydrate vapour into a flame and spraying them onto the apex of a silica target rod with the same device, to produce a material consisting of at least two components. The burner is a concentric five-fold tube structure quartz tube, and the components, the combustion gas, the inert gas for controlling the reaction, and the oxygen gas for the combustion are fed coaxially into the first, second, third, fourth and fifth layers of the burner respectively.

.../...

**Supplemental B x**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V.

The document does not disclose that the second component is atomised by means of gas substantially in the vicinity of the flame, which the application does

According to document D1 the essential technical features as stated in claims 1-3 and 5-7 are considered obvious for a person skilled in the art.

Claim 4

Document D1 further discloses that one component is silicon tetrachloride, and that the rare earth element could be Erbium.

Document D2 discloses that fused glass is prepared from a silicon compound, an aluminium compound in the form of a vapour, and a rare earth element in the form of a nitrate (see claim 1 and 3). The rare earth element is in the form of a solution, in which the solvent is an alcohol (see claim 4 and 5). The glass produced by the method, according to D2, is useful as a base material of optical fibre lasers and the like (see col. 1 line 10-15).

According to documents D1 and D2 in combination, it is considered obvious for a person skilled in the art to use a method as described in claim 4.

Conclusion

According to the above stated arguments, claims 1-7 are novel, are considered to have industrial applicability, but are considered to lack an inventive step.

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PPC10801/UH	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/FI99/00818	International filing date ( <i>day/month/year</i> ) 05.10.1999	Priority date ( <i>day/month/year</i> ) 05.10.1998
International Patent Classification (IPC) or national classification and IPC <sub>7</sub> C03B 37/018		
Applicant RAJALA, Markku et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of \_\_\_\_\_ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  02.05.2000	Date of completion of this report  19.12.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket      Telex Box 5055                                      17978 S-102 42 STOCKHOLM                      PATOREG-S Facsimile No. 08-667 72 88	Authorized officer  Mattias Arvidsson/MP Telephone No. 08-782 25 00

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/FI99/00818

## I. Basis of the report

1. With regard to the **elements** of the international application:\*

- ☒ the international application as originally filed
- ☐ the description:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the claims:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, as amended (together with any statement) under article 19  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the drawings:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the sequence listing part of the description:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.These elements were available or furnished to this Authority in the following language English which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☒ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims, Nos. \_\_\_\_\_
- ☐ the drawings, sheet/fig \_\_\_\_\_

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2 (c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI99/00818

**V. Reassessed statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims	<u>1-7</u>	YES
	Claims		NO
Inventive step (IS)	Claims		YES
	Claims	<u>1-7</u>	NO
Industrial applicability (IA)	Claims	<u>1-7</u>	YES
	Claims		NO

**2. Citations and explanations (Rule 70.7)**

The claimed invention relates to a method and device for spraying of a material in which a flame is produced by means of a fuel gas, and at least two different components are introduced to the flame in such a way that the components combine with each other, and form a material consisting of at least two components.

The following documents cited in the international search report, are documents of particular relevance:

D1: JP 4021536 WPI Derwent Abstract  
D2: US 5246475

Document D1 relates to a method for producing glass doped with rare earth element by feeding raw material glass and rare earth chloride vapour into flame and spraying on to a rotating silica target rod.

Document D2 relates to Method for preparing a fused silica glass body co-doped with a rare earth element and aluminium

Claims 1-3 and 5-7

Document D1 discloses feeding a glass starting material and atomised rare earth chloride hydrate vapour into a flame and spraying them onto the apex of a silica target rod with the same device, to produce a material consisting of at least two components. The burner is a concentric five-fold tube structure quartz tube, and the components, the combustion gas, the inert gas for controlling the reaction, and the oxygen gas for the combustion are fed coaxially into the first, second, third, fourth and fifth layers of the burner respectively.

.../...



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI99/00818

**Supplemental B x**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V.

The document does not disclose that the second component is atomised by means of gas substantially in the vicinity of the flame, which the application does

According to document D1 the essential technical features as stated in claims 1-3 and 5-7 are considered obvious for a person skilled in the art.

Claim 4

Document D1 further discloses that one component is silicon tetrachloride, and that the rare earth element could be Erbium.

Document D2 discloses that fused glass is prepared from a silicon compound, an aluminium compound in the form of a vapour, and a rare earth element in the form of a nitrate (see claim 1 and 3). The rare earth element is in the form of a solution, in which the solvent is an alcohol (see claim 4 and 5). The glass produced by the method, according to D2, is useful as a base material of optical fibre lasers and the like (see col. 1 line 10-15).

According to documents D1 and D2 in combination, it is considered obvious for a person skilled in the art to use a method as described in claim 4.

Conclusion

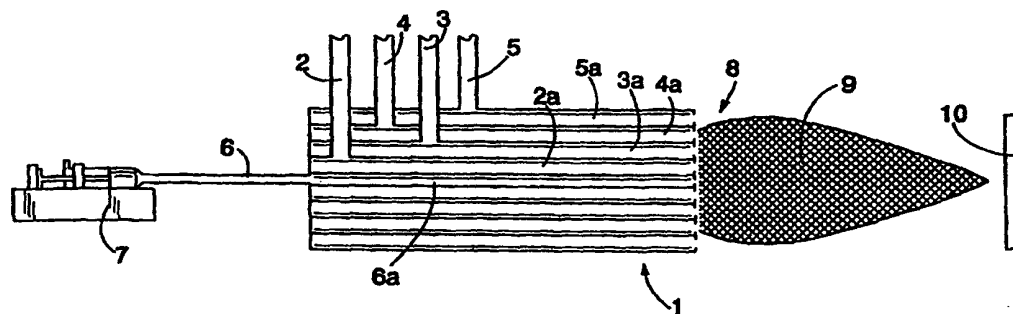
According to the above stated arguments, claims 1-7 are novel, are considered to have industrial applicability, but are considered to lack an inventive step.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C03B 37/018</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/20346</b> <b>(43) International Publication Date:</b> 13 April 2000 (13.04.00)
<b>(21) International Application Number:</b> PCT/FI99/00818 <b>(22) International Filing Date:</b> 5 October 1999 (05.10.99) <b>(30) Priority Data:</b> 982154 5 October 1998 (05.10.98) FI <b>(71)(72) Applicants and Inventors:</b> RAJALA, Markku [FI/FI]; Haapasaarentie 10 E 156, FIN-00960 Helsinki (FI). EEROLA, Markus [FI/FI]; Haapasaarentie 75, FIN-05470 Hyvinkää (FI). TIKKANEN, Juha [FI/FI]; Rautapellonkatu 37, FIN-33700 Tampere (FI). PITKANEN, Ville [FI/FI]; Elementinpolku 13 A 16, FIN-33720 Tampere (FI). <b>(74) Agent:</b> TAMPEREEN PATENTTITOIMISTO OY; Hermiankatu 6, FIN-33720 Tampere (FI).		<b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Finnish).</i>

(54) Title: METHOD AND DEVICE FOR SPRAYING OF A MATERIAL



## (57) Abstract

The invention relates to a method and a device for spraying of a material, wherein at least two different components are introduced into a flame (9) formed by means of a fuel gas in such a way that the components react with each other, forming multicomponent glass particles. By means of the flame (9), the multicomponent glass particles are sprayed to a desired target. The first component is introduced to the flame as a gas or a vapour, and the second component is introduced into the flame in liquid form and is atomized by means of a gas substantially in the vicinity of the flame. The first and second components are supplied into the flame (9) with the same device as the fuel gas. The liquid component and the gaseous component are formed into particles having the size in the order of magnitude of a nanometre and their mutual reaction is effected in such a way that homogeneous multicomponent glass particles are formed.

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**METHOD AND DEVICE FOR SPRAYING OF A MATERIAL**

The invention relates to a method for spraying of a material, in which method a flame is produced by means of a fuel gas, at least two different components are introduced to the flame in such a way that the components combine with each other and form a material consisting of at least two components.

Furthermore, the invention relates to a device for spraying of a material, which device comprises means for supplying a fuel gas in such a way that the fuel gas produces a flame, and means for introducing at least two different components to the flame in such a way that the components combine with each other and form a material consisting of at least two components, which can be sprayed to a desired target by means of the flame.

It is known to spray a solid substance with a flame spray device. In this method, the substance to be sprayed is fed to the flame spray gun in the form of solid particles which are sprayed by the flame spraying device to the desired target. When the particle size becomes smaller, the flame spray device is, however, easily soiled and clogged. Thus, it is difficult even to use the flame spray device to spray *e.g.* particles having a size of less than 20 micrometres, and the flame spray device is easily clogged and is expensive in its construction. Moreover, the solid matter to be sprayed is in several different phases during the flame spraying, being partly vapour, partly molten substance and substance molten in part, and when the substance is cooled, the final result is uneven.

US patent 3,883,336 presents a device in which silicon tetrachloride is supplied to a flame spray gun as a vapour by means of oxygen acting as a carrier gas. Further, said publication discloses that an aerosol is sprayed from outside to the flame of the flame spray gun to manufacture glass. However, the aerosol production requires a complex apparatus and, further, the aerosol formation requires that the viscosity of the liquid is within a certain range, which restricts the material combinations to be used. Moreover, the particles produced by the method are relatively large in size, *i.e.* in the order of magnitude of a micrometre.

Finnish patent 98832 presents a method and a device for spraying of a material, in which method the liquid substance to be sprayed is introduced to a flame formed with a fuel gas and is atomized with a gas substantially in the vicinity of the flame so that the atomization and the flame

formation take place in the same device. With said method, particles of the size of a nanometre can be produced in a simple and inexpensive way. However, the solution cannot be used to produce a material consisting of several components, *e.g.* multicomponent glass, with a controlled composition.

One application to produce multicomponent glass is the production of active fibres. In the production of active fibres, the glass material must be doped with rare earth metals, for example erbium. Erbium is not available as a liquid whose vapour pressure would be sufficiently low so that active fibres could be produced by conventional fibre production methods without extensive and expensive modification of the process. For this reason, the generally used method for producing active fibre is to manufacture a porous preform which substantially consists of amorphous silicon dioxide. The preform is immersed in a liquid containing erbium. After the impregnation of several hours, the preform is dried and sintered, thereby giving a doped fibre preform. The demerits of the method include indefiniteness of the doping quantity and clustering of the substance, which impairs the properties of the final product obtained. Furthermore, active fibre can be produced with an aerosol process, in which an erbium-containing aerosol is produced by an ultrasound method. The aerosols produced separately by the ultrasound method are led into a thermal reactor where they react to produce multicomponent glass. The drawbacks of this method are its complexity, difficulties in the doping, and the large size of the particles produced, that is, the particle size is in the order of magnitude of about one micrometre.

It is an aim of the present invention to provide a method and a device whereby the above-mentioned drawbacks can be avoided.

The method according to the invention is characterized in that the first component is introduced to the flame in a gaseous or vaporous form and the second component is introduced to the flame in a liquid form and is atomized by means of a gas substantially in the vicinity of the flame, and that both the first component and the second component are supplied to the flame with the same device as the fuel gas.

Further, the device according to the invention is characterized in that the device has a gas tube for introducing the first component to the flame in a gaseous or vaporous form, a liquid tube for introducing the second component to the flame in a liquid form, and a gas tube for introducing an atomizing gas to the vicinity of the liquid tube for atomizing the liquid

component substantially in the vicinity of the flame, wherein both the first component and the second component are arranged to be supplied to the flame with the same device as the fuel gas.

5 The essential idea of the invention is that at least two different components are led to the flame and that the first component is led to the flame as a gas or as a vapour, and the second component is led to the flame in liquid form and is atomized by means of a gas substantially in the vicinity of the flame, and that the first and second component are fed to the flame together with the fuel gas with the same device. Thus, the liquid component  
10 and the gaseous component are formed into particles having a size in the order of magnitude of a nanometre, and their mutual reaction is accomplished in such a way that for example homogeneous multicomponent glass particles are formed. The produced particles can be further guided by means of the flame onto the surface of various materials, or they can be collected  
15 as separate particles with a suitable device, for example to produce active fibre.

The advantage of the invention is the capability to produce, in a very simple and inexpensive way, very fine and homogeneous particles consisting of at least two components, such as multicomponent glass particles.

20 The invention will be described in more detail in the appended drawing, in which

Fig. 1 shows schematically the entity of a flame spray device according to the invention in a side view, and

25 Fig. 2 shows schematically a nozzle part of the device according to the invention in a front view.

Figure 1 shows a flame spray device according to the invention. A flame spray gun 1 is used to form a flame 9 to spray a material. The required gases are supplied to the flame spray gun 1 along gas ducts 2, 3, 4 and 5. Along the gas ducts 2—5 are supplied the fuel gases forming the  
30 flame, the atomizing gas for the liquid to be sprayed, one component, in gas or vapour form, of the material consisting of at least two components, such as multicomponent glass, and possibly a gas to be produced for controlling the reaction. The number of the gas ducts 2—5 is naturally sufficient according to the number of gases that need to be supplied to the flame spray  
35 gun 1. The second component of the multicomponent glass to be formed is supplied in liquid form to the flame spray gun 1, along a liquid duct 6. The liquid is transferred along the liquid duct 6 by pumping it for example with an

injection pump 7. The transfer of the liquid along the liquid duct 6 can also be implemented for example by supplying the liquid from a pressure tank or in another way known as such.

At the right end of the flame spray gun 1, seen in Fig. 1, there is a nozzle 8 where the fuel gases are ignited to produce a flame and where the liquid is atomized by means of an atomizing gas. The atomizing takes place substantially in the vicinity of the flame 9. Thus, the liquid component can be atomized into very fine particles, having a size in the order of magnitude of about one nanometre. Similarly, equally small particles can be formed of the gaseous or vaporous component. Both components are fed into the flame together with the fuel gas with the same device. Preferably, the feeding of the fuel gas, the feeding of the first component and the feeding of the second component into the flame is implemented with one and the same device, that is, via a common nozzle 8, as is shown in Fig. 1. It is thus very easy to direct the multicomponent glass particles to be sprayed to the target 10. The particles of the first and second component react with each other, forming homogeneous multicomponent glass particles. The multicomponent glass particles can be further directed by means of the flame 9 onto the surface of various materials, or they can be collected as separate particles using a suitable device.

The liquid component of the multicomponent glass is brought to the flame spray gun 1 along the liquid duct 6. From the liquid duct 6, the liquid is transferred to a liquid tube 6a in the centre of the flame spray gun 1. Along the first gas duct 2, the gas for atomizing the liquid is introduced into a first gas tube 2a surrounding the liquid tube. Along the second gas duct 3, a second gas is introduced into a second gas tube 3a surrounding the first gas tube 2a. Furthermore, along the third gas duct 4, a third gas is introduced into a third gas tube 4a surrounding the second gas tube 3a, and along the fourth gas duct 5, a fourth gas is introduced into a fourth gas tube 5a surrounding the third gas tube 4a. The liquid tube 6a and the first, second, third and fourth gas tubes 2a, 3a, 4a, and 5a are thus coaxial tubes within each other. The gas flowing from the first gas tube 2a in the nozzle 8 atomizes the liquid flowing along the liquid tube 6a into droplets.

The liquid component of the multicomponent glass to be formed can be a suitable aqueous or alcohol solution of the desired ion. For example in the production of active fibre, *i.e.* light intensifying fibre, it is possible to use a solution containing erbium nitrate, water or alcohol and a form of alu-

minium which is soluble in water or alcohol. Along the second gas duct 2 can be supplied for example hydrogen which atomizes the liquid in the nozzle 8. Along the second gas duct 3 can be supplied silicon or germanium tetrachloride in gaseous or vaporous form, and along the third gas duct 4 oxygen can be brought. After the nozzle 8, hydrogen and oxygen react to form a flame 9. The precise process of the reactive formation in the flame is unclear, but it can be assumed in practice that the silicon or germanium tetrachloride reacts by forming very small silicon dioxide or germanium dioxide particles, and the liquid particles react by forming erbium and aluminium oxide. The formed particles react either simultaneously or separately with the above-mentioned reactions and combine with each other to form homogeneous multicomponent glass. The produced multicomponent glass particles are guided by means of the flame 9 onto the surface of a target 10, which in the manufacture of an active fibre is a mandrel, whereby the multicomponent glass particles form a porous glass surface on the mandrel surface. On the mandrel surface it is possible to accumulate several different glass layers whose material composition can be altered in a simple manner, if necessary. After the accumulation, the mandrel can be removed, and the produced preform is sintered in a manner known as such from the manufacturing process of an optical fibre.

The fourth gas duct 5 and the respective fourth gas tube 5a are not necessary. However, they can be used when desired for improving the reaction control, for example by feeding *e.g.* argon or another suitable protective gas along the fourth gas duct 5 and further along the fourth gas tube 5a. The protective gas prevents the effect of external oxygen in the reaction.

It should be noted that in Fig. 1, the structure of the flame spray gun 1 is presented, for clarity, in a scale larger than the real situation. For effective atomization, it is preferable to make *e.g.* the velocity of the spraying gas as high as possible. Thus, the holes of the nozzle 8 should be made sufficiently small. Furthermore, the structure of the liquid tube 6a and the first gas tube 2a can be described so that said tubes are structurally two hollow needles placed one inside the other.

Figure 2 shows the nozzle 8 seen in a front view. Figure 2 shows the hole at the end of the liquid tube 6a coming along the centre of the nozzle 8. The hole of the first gas tube 2a can be seen around this hole. The gas flowing along the second gas tube 3a is shown to be introduced through the



nozzle 8 via orifices 11. In a corresponding manner, the gas flowing along the third gas tube 4a is introduced through the nozzle 8 via orifices 12, and the gas flowing along the fourth gas tube 5a is led through the nozzle 8 via orifices 13. The size and geometry of the holes and orifices of the nozzle 8 may vary in a desired manner, but it is essential that the velocity of the liquid and the atomizing gas in the nozzle 8 can be adjusted as desired so that the liquid can be formed into sufficiently small droplets to allow sufficiently small particles to be produced and, on the other hand, to provide sufficient velocity of the gases forming the flame 9.

The drawing and the related description are only intended to illustrate the idea of the invention. In details, the invention may vary within the scope of the claims. Consequently, the location and order of the liquid tube and the gas tubes may vary in a desired way. Furthermore, the fuel gas can consist, in the above-described manner, of two or more gases to be supplied along separate gas tubes to the nozzle 8, or the fuel gas used can be a gas or gas mixture supplied along one gas tube to the nozzle 8, such as a mixture of oxygen and acetylene.

## CLAIMS

1. A method for spraying of a material, in which method a flame (9) is produced by means of a fuel gas, at least two different components are introduced to the flame (9) in such a way that the components combine with each other and form a material consisting of at least two components, **characterized** in that the first component is introduced to the flame (9) in a gaseous or vaporous form and the second component is supplied to the flame (9) in liquid form and is atomized by means of a gas substantially in the vicinity of the flame (9), and that both the first component and the second component are supplied to the flame (9) with the same device as the fuel gas.
2. The method according to claim 1, **characterized** in that the first component, the second component and the fuel gas are supplied to the flame (9) by the same device.
3. The method according to claim 2, **characterized** in that the first component, the second component and the fuel gas are supplied to the flame (9) coaxially.
4. The method according to any of the preceding claims, **characterized** in that the first component is silicon or germanium tetrachloride and the second component is a solution containing erbium nitrate, water or alcohol, and a form of aluminium which is soluble in water or alcohol, in such a way that multicomponent glass particles can be formed to manufacture active fibre.
5. A device for spraying of a material, which device comprises means for introducing a fuel gas in such a way that the fuel gas produces a flame (9), and means for introducing at least two different components to the flame (9) in such a way that the components combine with each other and form a material consisting of at least two components, which can be sprayed to a desired target by means of the flame (9), **characterized** in that the device has a gas tube (3a) for introducing the first component to the flame (9) in a gaseous or vaporous form, a liquid tube (6a) for introducing the second component to the flame (9) in a liquid form, and a gas tube (2a) for introducing an atomizing gas to the vicinity of the liquid tube for atomizing the liquid component substantially in the vicinity of the flame (9), wherein both the first component and the second component are arranged to be supplied to the flame (9) with the same device as the fuel gas.

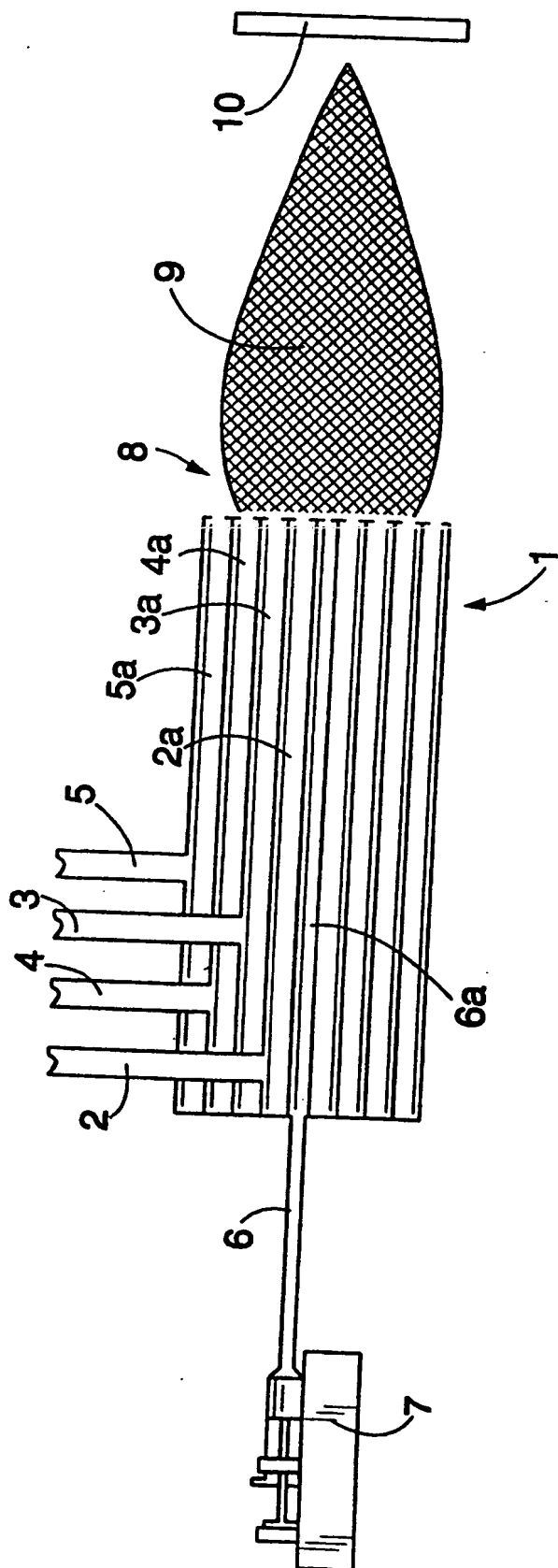
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6. The device according to claim 5, **characterized** in that the device comprises a nozzle (8) and that the device comprises means for supplying the first component, the second component and the fuel gas into the flame (9) via a common nozzle (8).

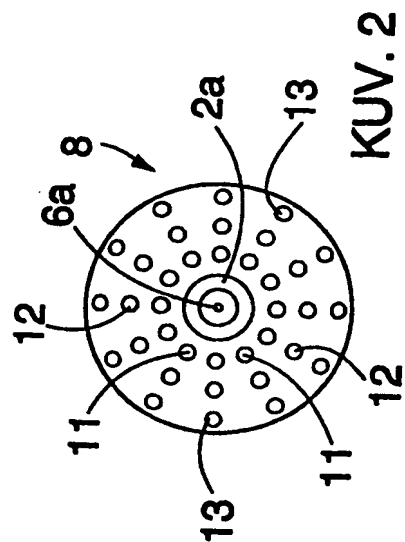
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7. The device according to claim 6, **characterized** in that the means for supplying the first component, the second component and the fuel gas into the flame (9) are arranged coaxially.

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KUV.1



KUV.2

1  
INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00818

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C03B 37/018

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C03B, G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PAJ, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 4021536 A (HITACHI CABLE LTD) 24 January 1992 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 2000-02-08) Retrieved from: EPO WPI Database. DW199210, Accession No. 1992-076651; & JP 4021536 (HITACHI CABLE LTD) 1992-01-24(abstrac) (online)(retrieved on 2000-02-08). Retrieved from: EPO PAJ Database.	1-3,5-7
Y	--	4
Y	US 5246475 A (NOBORU EDAGAWA ET AL), 21 Sept 1993 (21.09.93), figure 1, claims 1,3-5, abstract	4
A	figure 1, claims 1,3-5, abstract --	1-3,5-7

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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2  
INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DE 19725955 C1 (HERAEUS QUARZGLAS GMBH), 21 January 1999 (21.01.99), column 2, line 4 - column 12, line 55, figure 1, claims 1-7, abstract	1-3,5-7
A,P	abstract --	4
A	FI 98832 B (TIKKANEN, JUHA), 15 May 1997 (15.05.97), claims 1-3,6, abstract --	1-7
A	EP 0463783 A1 (AMERICAN TELEPHONE AND TELEGRAPH COMPANY), 2 January 1992 (02.01.92), column 5, line 7 - line 12, figures 3,4, claims 1-5,8,9, abstract -- -----	1-7

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

02/12/99

PCT/FI 99/00818

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